

Partly Occupied Wannier Functions

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We introduce a scheme for constructing partly occupied, maximally localized Wannier functions (WFs) for both molecular and periodic systems. Compared to the traditional occupied WFs the partly occupied WFs possess improved symmetry and localization properties achieved through a bonding-antibonding closing procedure. We demonstrate the equivalence between bonding-antibonding closure and the minimization of the average spread of the WFs in the case of a benzene molecule and a linear chain of Pt atoms. The general applicability of the method is demonstrated through the calculation of WFs for a metallic system with an impurity: a Pt wire with a hydrogen molecular bridge.

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The idea of representing the electronic ground state of a solid-state system in terms of localized orbitals dates back to Wannier [1] who introduced a canonical transformation between the Bloch states of an insulating crystal and a set of localized functions. These localized Wannier functions (WFs) provide a formal justification of the widely used tight-binding [2] and Hubbard models [3]. A scheme for evaluation of maximally localized WFs for composite bands has been developed by Marzari and Vanderbilt [4], and the WFs have turned out to be useful in a number of contexts including electron transport calculations [5], linear-scaling electronic structure methods [6], and in the theory of electric polarization [7, 8].

In the context of molecular systems the analogous of Wannier functions for finite systems has been studied under the name "localized molecular orbitals" [9, 10, 11, 12, 13, 14]. These are traditionally defined by an appropriate unitary transformation of the occupied single-particle eigenstates and represent a strong analysis tool as they provide insight into chemical properties such as bond types, coordination, and electron lone pairs. In the following we shall for simplicity use the term WF to cover also localized molecular orbitals.

In this letter we demonstrate that in constructing localized WFs it is in some cases advantageous to consider not only the space of occupied states but to include also selected unoccupied states through a bonding-antibonding closing procedure. The changes achieved by the bonding-antibonding closing can be viewed directly in Fig. 1 where calculated WFs with and without the inclusion of additional unoccupied states are shown in the case of a benzene molecule. In the upper panel only the occupied states are used and some of the resulting WFs clearly mix σ - and π -character. By including three selected unoccupied states the resulting partially occupied WFs become more localized and the σ - and π -systems are now separated. In addition the rotational symmetry of the molecule is more clearly reflected by the partly

occupied WFs.

The problem solved by the bonding-antibonding closing is the following: if we consider two well-localized atomic orbitals on neighboring atoms in a molecule and allow the two states to hybridize, a bonding and an antibonding combination will result – combinations which may be less localized than the individual atomic orbitals. To regain the localized atomic orbitals from the molecular orbitals we need both the bonding and the antibonding combination independent of their occupation. In some cases the antibonding state may have hybridized further with other states and the state which "matches" the bonding state will be a linear combination of eigenstates. To apply the bonding-antibonding closing in practice a systematic scheme to identify the relevant unoccupied states is clearly required. We show that this can be

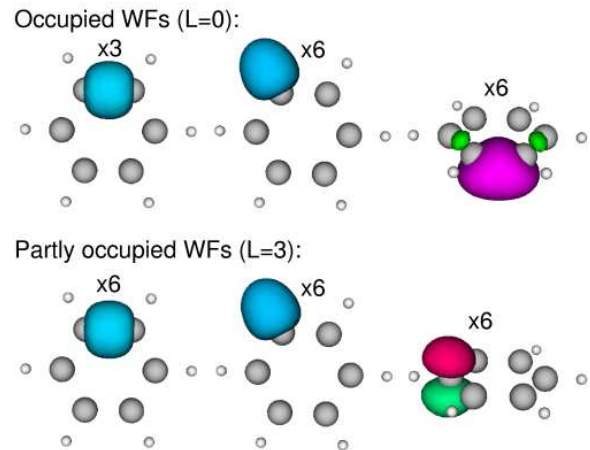


FIG. 1: Occupied and partly occupied Wannier functions for benzene C_6H_6 . The traditional (occupied) WFs are seen to mix the σ and π orbitals. Inclusion of the three antibonding π orbitals leads to the partly occupied WFs which are more localized and separate the orbitals with different mirror symmetry.

achieved by optimizing the localization of the resulting WFs.

The lack of localization of WFs obtained if only occupied states are considered is well-known in the case of extended metallic systems [15, 16]. A proper localization of the WFs requires in this case completion of the partly occupied valence bands (the analogue of bonding-antibonding closing for a periodic system) which may be difficult due to crossings and mixing of the valence bands with unwanted higher-lying bands. This problem was addressed by Souza, Marzari, and Vanderbilt [15] who constructed a disentangling procedure which makes it possible to follow a given band by minimizing the change in character of the Bloch states across the Brillouin zone. In this way the relevant unoccupied states could be identified. The approach we suggest here makes no reference to the wave vector, it is simple to apply and valid for both isolated and periodic systems.

We note that different techniques for constructing localized orbitals have been developed in connection with linear scaling electronic structure methods [6]. In that context the orbitals are typically constructed during an electronic structure calculation and are required to vanish outside predefined localization regions. In contrast, the scheme we propose is an exact transformation of already determined eigenstates to obtain maximal localization.

Our starting point is a set of single-particle eigenstates $\{\psi_n\}$ obtained for example from a Density Functional Theory (DFT) [17] calculation. We denote the total number of eigenstates included in the DFT calculation by N and the number of occupied eigenstates by M . Following Marzari and Vanderbilt [4] we measure the spread of the WFs $\{w_n\}$ by the sum of second moments

$$S = \sum_n (\langle w_n | r^2 | w_n \rangle - \langle w_n | \mathbf{r} | w_n \rangle^2). \quad (1)$$

The WFs are expanded in terms of the M occupied eigenstates and L extra degrees of freedom (EDF) $\{\phi_l\}$ from the $(N-M)$ -dimensional space of unoccupied eigenstates. This will lead to a total of $M+L$ WFs and we thus require $N \geq M+L$. The expansion takes the form

$$w_n = \sum_{m=1}^M U_{mn} \psi_m + \sum_{l=1}^L U_{M+l,n} \phi_l, \quad (2)$$

where the unoccupied orbitals are written as

$$\phi_l = \sum_{m=1}^{N-M} c_{ml} \psi_{M+m}. \quad (3)$$

The columns of the matrix c are taken to be orthonormal and represent the coordinates of the EDF with respect to the unoccupied eigenstates. The matrix U is unitary and represents a rotation in the space of the functions $\{\psi_1, \dots, \psi_M, \phi_1, \dots, \phi_L\}$. Through the expansions (2)

and (3), S becomes a function of U_{ij} and c_{ij} , which must be minimized under the constraint that U is unitary and the columns of c are orthonormal.

To keep technicalities at a minimum the formulation given above has been specialized to systems which are either isolated or described in a periodically repeated supercell in the Γ -point approximation. A detailed account of the method including the \mathbf{k} -point formulation will be given elsewhere [18]. Here we focus on the case of a cubic supercell of length a in the Γ -point approximation. Extension of the theory to supercells of general symmetry is straightforward along the lines of Refs. 19 and 13.

In the limit of a large supercell, minimizing S is equivalent to maximizing the functional [13, 20]

$$\Omega = \sum_n (|X_{nn}|^2 + |Y_{nn}|^2 + |Z_{nn}|^2), \quad (4)$$

where the matrix X is defined as $X_{nm} = \langle w_n | e^{-i(2\pi/a)x} | w_m \rangle$, with similar definitions for Y_{nm} and Z_{nm} . The unitary matrix at iteration n is written as $U^{(n)} = U^{(n-1)} \exp(-A)$, where A is an anti-hermitian matrix. By straightforward differentiation we obtain expressions for the gradients $\partial\Omega/\partial A_{ij}$ and $\partial\Omega/\partial c_{ij}^*$ giving the steepest uphill direction of Ω upon variations in A and c . The orthonormality constraint on c is invoked through a set of Lagrange multipliers. Any gradient-based optimization scheme can now be applied to maximize Ω .

Given N and L , the algorithm introduced above produces the $M+L$ most localized WFs. We shall assume that N has been fixed at a value large enough to include all anti-bonding states relevant for the localization. The problem is then to determine a good value for L . It seems as a natural strategy to choose an L that gives a high localization *per* orbital. To quantify this statement we define the average localization per orbital as

$$\langle \Omega \rangle = \frac{\Omega}{M+L}, \quad (5)$$

where $M+L$ is the total number of WFs. From the definition of Ω it is clear that $0 \leq \langle \Omega \rangle \leq 3$. Fixing L on the basis of $\langle \Omega \rangle$ represents a quite general criterion which can be applied to any system. However, the localization procedure must be carried out for several L which might be a tedious task depending on the size of the system. Formally the global maximum of $\langle \Omega \rangle$ is attained in the limit where both N and L tend to infinity in which case completely localized delta functions can be realized. However, we have found that for practical values of N where very high energy states are not considered, $\langle \Omega \rangle$ goes through a local maximum as L is increased beyond 0. For many systems it is possible to determine a value for L based on symmetry arguments, chemical intuition, or a closed band condition. In particular the latter strategy is natural for crystalline systems where the closed

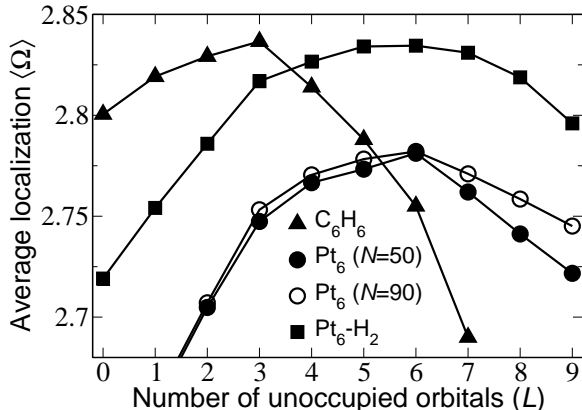


FIG. 2: Average localization per Wannier function as a function of the number of included unoccupied orbitals for the three systems studied. For the benzene molecule the maximum appears at $L = 3$ corresponding to the inclusion of the three antibonding π orbitals. For the Pt chain the maximum at $L = 6$ corresponds to completion of the valence bands. (The values of $\langle\Omega\rangle$ do not compare from one system to another due to dependence on the size of the supercell.)

band condition is satisfied by choosing L equal to the number of unoccupied states belonging to all partly occupied bands. As we shall see in the following examples the two criteria for determining L lead to similar results.

All the following calculations are based on the Kohn-Sham eigenstates as defined within DFT [17]. We use a plane wave based pseudopotential code [21] with an energy cutoff of 25 Ry for the plane wave expansion and describe the ion cores with ultrasoft pseudopotentials [22].

We have constructed the maximally localized WFs of an isolated benzene molecule in a cubic supercell of length $a = 16$ Å. If we consider only the occupied eigenstates of benzene, corresponding to $L = 0$ in the method, we find the 15 occupied WFs shown in the upper panel of Fig. 1. Nine of these are σ -bonds centered at each C-H and every second C-C bond, and the last six orbitals are double bonds with a mixed σ - and π -character centered at the three remaining C-C bonds. This is the classical picture of the chemical bonds in benzene. In this picture the resulting orbitals apparently break the six-fold rotational symmetry of the molecule, i.e. the bonding orbitals between different C-C pairs differ. Moreover, the planar structure of the molecule suggests a separation of σ - and π -orbitals contrary to C-C double bonds. The occupied subspace spanned by all the WFs of course possesses the full symmetry.

The lack of symmetry in the chemical picture of benzene is a result of ignoring the three anti-bonding π -orbitals of the C ring in the construction of the WFs. In Fig. 2 (triangles) we plot the average localization of the WFs for various L values. The maximum occurs

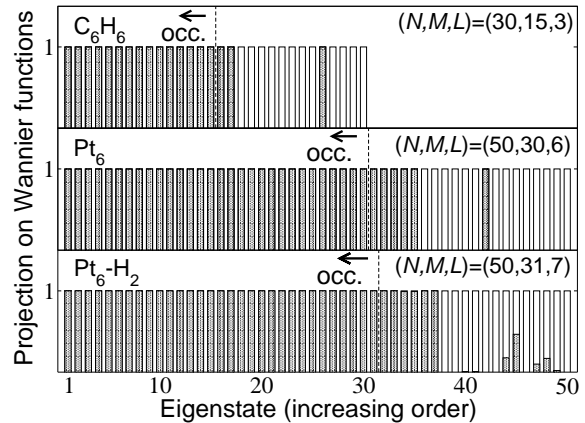


FIG. 3: The norm of the projection of eigenstates onto the subspace spanned by the partly occupied WFs for the three systems studied. The eigenstates are listed in increasing order according to their energy. States below the dashed line are occupied. It is seen that in the case of the benzene molecule and the Pt chain the algorithm selects particular unoccupied states necessary for the bonding-antibonding closing. In the case of the hydrogen molecule in the Pt chain one of the WFs has weight on an unoccupied resonance distributed over several eigenstates.

for $L = 3$. To analyze the composition of the EDF we have projected the molecular eigenstates onto the WFs generated with $L = 3$, see upper panel of Fig. 3. By inspection we have verified that the EDF selected by the algorithm are exactly the three anti-bonding π -orbitals of the C ring. Maximizing $\langle\Omega\rangle$ is therefore equivalent to performing a bonding-antibonding closure. The 18 partly occupied WFs obtained with $L = 3$ consist of σ -bonds at all C-H and C-C pairs and a p -orbital perpendicular to the molecular plane centered at each C atom (lower panel of Fig. 1). Consequently, the inclusion of 3 EDF restores the rotational symmetry and separates σ - and π -orbitals.

We have performed a similar analysis for a linear chain of six Pt atoms with periodic boundary conditions (Pt₆), see Fig. 4(1a). Such monatomic chains have been produced and studied in STM experiments [23] and by the mechanically controlled break junction technique [24].

The valence bands of an infinite Pt wire consist of five d - and one s -band. For each band only six Bloch states comply with the boundary conditions in Pt₆ and consequently it takes a total of 36 states to close the bands. Since there are 30 occupied states, the closed band condition can thus be fulfilled with $L = 6$. From Fig. 2 (circles) we see that the closed band condition coincides with the maximum of $\langle\Omega\rangle$. In the middle panel of Fig. 3 we show the projection of eigenstates onto the Wannier functions corresponding to $L = 6$. By comparing with

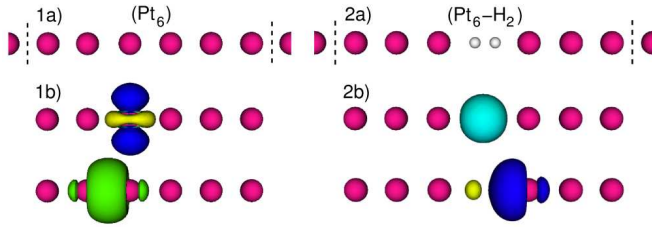


FIG. 4: Partly occupied Wannier functions for a periodically repeated, linear string of 6 Pt atoms without and with an inserted hydrogen bridge. The WFs have been generated with $L = 6$ (Pt_6) and $L = 7$ ($\text{Pt}_6\text{-H}_2$). The WFs shown for the $\text{Pt}_6\text{-H}_2$ system correspond to H_2 and H-Pt σ -bonds.

the band diagram of the Pt wire, we find a perfect match between the EDF and the unoccupied Bloch states of the valence bands. Again this shows that closing the bands is equivalent to minimizing the average spread. For $L = 6$ we find five atom-centered d -orbitals, of which one is shown, and one σ -orbital centered between each Pt-Pt pair. The transformation to WFs allows for explicit extraction of tight-binding parameters. For example, the doubly degenerate δ -band of the Pt chain is characterized by the hopping parameters (in eV) $t_1 = 1.08$, $t_2 = 0.13$, $t_3 = 0.03$.

When N is increased from 50 to 90 the localization generally improves due to the larger space available for the EDF, see Fig. 2 (open circles). If we increase N further this trend would continue and eventually the maximum would start shifting towards larger L values. In the limit $N \rightarrow \infty$ $\langle \Omega \rangle$ would increase monotonically as a function of L . This shift of the maximum, however, occurs only when N becomes very large, i.e. when high-energetic and chemically irrelevant states enter the localization space.

As a final example we analyze the effect on the WFs when a molecular hydrogen bridge is inserted in the Pt_6 system, see Fig. 4(2a). A molecular hydrogen bridge between Pt contacts has recently been realized and studied experimentally [25]. The average localization has a maximum for $L = 6$. The maximum is, however, not very pronounced and its position depends on the Pt-H and H-H bond lengths. Consequently we have studied the WFs for $L = 5, 6, 7$. In all three cases we recover the five d -orbitals per Pt found for Pt_6 . The σ -orbitals are slightly distorted and the one in the bridge region is replaced by: an H_2 bonding orbital ($L = 5$), two s -orbitals located symmetrically on each H atom ($L = 6$), an H_2 bonding orbital and two Pt-H bonds with σ symmetry ($L = 7$). The latter situation is shown in Fig. 4(2b). As can be seen from the lower panel of Fig. 3 this system provides an example where one of the EDF is a superposition of eigenstates.

To conclude we have proposed a method for finding maximally localized, partly occupied WFs. The method ensures by construction that any occupied eigenstate can

be expanded in terms of the obtained WFs. The inclusion of additional unoccupied states in the definition of the WFs improves the localization and simplifies the resulting chemical pictures. The method can easily be modified so that not the occupied states but for example the states in an energy window around the Fermi level are exactly represented. Extra high- and low-energy states can then be included to construct effective model Hamiltonians for the states around the Fermi level.

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